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## An Apparatus for Measuring Flow-Induced Crystallization of Polymers

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Requirements of an apparatus for measuring flow-induced crystallization of polymers were discussed on the basis of a nonisothermal crystallization theory. Results of calculation with a computer indicated that the thickness of a specimen with relatively large heat of crystallization should be less than 0.05 mm to observe rapid crystallization process which would complete in, say, one second. Then, a special apparatus was designed and constructed to fulfill the requirements. With this apparatus, it was possible to heat a thin polymer specimen between beryllium plates (50  $\mu$  thick) above its melting point, quench the specimen to a crystallization temperature, and then deform the super-cooled specimen by loading one of the beryllium plates with a weight. The process of crystallization was observed by X-ray method, and the displacement of the plate was recorded by means of a differential transformer. From these data, we obtained the degree of crystallinity and the shear strain as functions of time. Some results on the flow-induced crystallization of a polyethylene (Sholex 6009) were also illustrated.

### INTRODUCTION

The crystallization of polymers from an oriented state of molecular chains has been an important subject in the field of polymer physics, and several problems on the phenomenon still remain to be solved. For example, the mechanism of generation of structure and the kinetics of crystallization in the course of solidification from oriented melts are not yet fully understood. Quantitative studies of the phenomenon in noncrosslinked polymers are especially few, because of the difficulty in maintaining constant molecular orientation in polymer melts. The present paper deals with some problems on an apparatus for measuring flow-induced crystallization.

Whereas temperature is a unique parameter prescribing crystallization conditions from quiescent melts, a new parameter representing a preferred orientation of molecular chains should be necessary to prescribe those from oriented melts. For this purpose the most suitable one will be the orientation factor of molecular axis along the flow direction. Unfortunately, this factor varies remarkably during crystallization,<sup>1,2)</sup> and it is practically impossible to adjust experimental conditions so as to keep this factor constant. A condition of constant stress is easily realized in experiment (especially in the case of shear flow), and often met in the course of commercial polymer processing. Therefore, an apparatus for measuring flow-induced crystallization was designed to meet the conditions under which the crystallization proceeded isothermally under a constant shear stress.

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Various experimental conditions and methods appeared in literature and conceivable ones to achieve this purpose are listed in Table I. Each method has its

Table I. Variations in Flow-Induced Crystallization Experiments

Type of strain	Shear strain, elongational strain
Mode of strain or stress	Constant strain rate, instantaneous strain, constant stress, constant tension
Apparatus	Coaxial cylinders, parallel plates, cone and plate, spinning apparatus, drawing apparatus
Temperature	Isothermal, nonisothermal
Physical quantity or method used for crystallinity measurement	Specific volume, stress, strain, heat of crystallization, X-ray diffraction, microscopic observation, light scattering
Physical quantity or method used for orientation measurement	Birefringence, X-ray diffraction

advantages and disadvantages. If a specimen chamber of coaxial cylinder type is used, the specimen can be strained without limitation between the coaxial cylinders before crystallization starts. However an optical measurement is very difficult, and the large heat capacity of the system impedes quick quenching of the specimen. On the other hand, a strain is limited in the case of a parallel plate system, which might impose some restrictions on crystallization conditions. The advantage is the reduction of heat capacity of the system. The details of some experiments on this topic appeared in literature are also summarized in Table II.

Table II. List of Details of Some Experiments

Authors	Kobayashi, Nagasawa <sup>3)</sup>	Krueger, Yeh <sup>4)</sup>	Haas, Maxwell <sup>5)</sup>	Wereta, Gogos <sup>6)</sup>	Katayama, Amano, Nakamura <sup>1)</sup>
Type of strain	Shear	Shear	Shear	Shear	Elongational
Mode of strain or stress	Constant strain rate	Constant strain rate	Constant stress	Instantaneous strain	Constant tension
Apparatus	Coaxial cylinders	Coaxial cylinders	Parallel plates	Parallel plates	Spinning apparatus
Temperature	Nonisothermal	Isothermal	Isothermal	Isothermal	Nonisothermal
Physical quantity or method used for crystallinity measurement	Stress	Stress, volume	Strain, microscopic observation	Stress, volume	X-ray diffraction
Physical quantity or method used for orientation measurement	—	—	—	—	X-ray pattern, birefringence

## REQUIREMENTS OF AN APPARATUS

It is a well-known fact that the rate of crystallization of a polymer increases immensely when the polymer crystallizes from an oriented state. An apparatus will spoil its usefulness unless it enables the measurement of rapid crystallization under prescribed conditions. The problem in satisfying the isothermal condition is how to suppress the temperature rise in a polymer specimen due to the heat of crystallization. An estimation of the temperature rise is following.

The enthalpy change per unit volume per unit time can be expressed by:

$$\rho \frac{\partial H}{\partial t} = K_c \nabla^2 T + W$$

where  $\rho$ =density,  $H$ =enthalpy per unit mass,  $t$ =time,  $K_c$ =thermal conductivity,  $T$ =temperature, and  $W$ =heat generation rate per unit volume due to deformation.

Since enthalpy is a function of temperature and the degree of crystallinity  $X$  which was defined previously,<sup>8,9</sup> the above equation becomes

$$\rho c_p \frac{\partial T}{\partial t} - \rho \Delta H \frac{\partial X}{\partial t} = K_c \nabla^2 T + W \quad (1)$$

where  $c_p$ =specific heat at constant pressure, and  $\Delta H$ =heat of crystallization.

Another fundamental equation to calculate the temperature rise is concerned with the kinetics of crystallization under nonisothermal conditions. Assuming that the kinetics of crystallization at a constant temperature  $T$  under a constant stress  $\tau$  is expressed by

$$X = 1 - \exp \{ -k(T, \tau) t^n \}$$

which is a kind of the Avrami equation, we expect the following equation in the case of nonisothermal crystallization under constant stress  $\tau$  on the analogy of the kinetics of nonisothermal crystallization from quiescent melts.<sup>8</sup> That is,

$$X = 1 - \exp \left\{ - \left( \int_0^t K(T, \tau) dt \right)^n \right\} \quad (2)$$

where  $K(T, \tau) = \{k(T, \tau)\}^{1/n}$ , and  $T$  is a function of time. The simultaneous solution of Eqs. (1) and (2) under given initial and boundary conditions gives the degree of crystallinity and temperature at any moment in the course of crystallization. In order to proceed to a numerical calculation on a process of crystallization, we assume that an imaginary polymer (which resembles a kind of polyethylene) has a temperature dependence of the crystallization half time  $t_{1/2}$ , under a certain stress  $\tau$ , expressed by

$$\frac{1}{t_{1/2}} = \exp \left( A - \frac{T}{B} - \frac{CT_m}{T(T_m - T)} \right),$$

or

$$K(T, \tau) = \frac{(\ln 2)^{1/n}}{t_{1/2}}$$

where  $A=16$ ,  $B=3000$ ,  $C=200$ , and  $T_m=423$  ( $^{\circ}K$ ). Then, we consider a spec-

imen placed between two parallel plates shown in Fig. 1. The plates are thin glass slides when an optical measurement is made, and beryllium plates attached to brass bases when an X-ray measurement is made. A calculation was carried out on the system of Fig. 1 immersed in hot air stream of a constant temperature. The procedure and assumptions for the calculation of degree of crystallinity and temperature in the specimen at any moment were essentially the same as those used in the analysis of melt spinning process,<sup>8)</sup> and the following constants were adopted:

$$H=40 \text{ cal/g, } \rho=0.833 \text{ g/cm, } c_p=0.55 \text{ cal/g-deg,}$$

$$K_c=8.7 \times 10^{-4} \text{ cal/cm-sec-deg, and } n=1.$$

Some results of the calculation are illustrated in Figs. 2~4. Figure 2 shows the

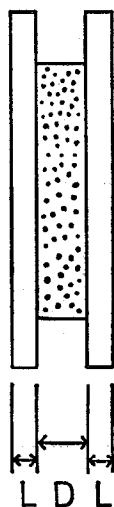


Fig. 1. A polymer specimen placed between parallel plates.

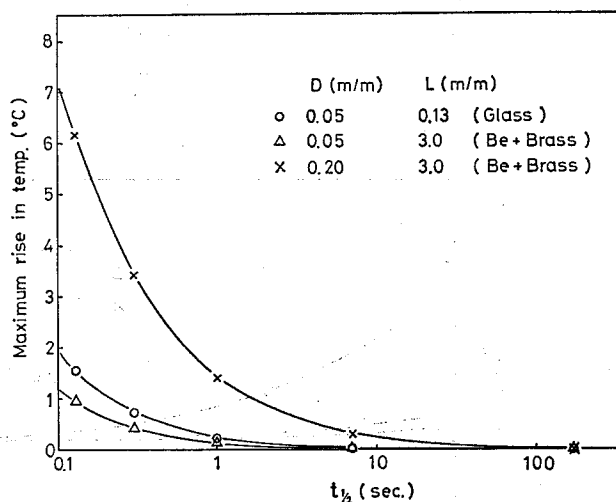


Fig. 2. Calculated maximum temperature rise in the course of crystallization.

maximum temperature rise in the course of crystallization in three cases. The temperature rise in the region of rapid crystallization is appreciable when the thickness of a specimen is large. Figure 3 shows the degree of crystallinity and temperature distributions in the specimen at the time when the maximum rise in temperature occurs at the center of the specimen (the average degree of crystallinity reaches about 0.56). The ratio of the calculated crystallization half time ( $t'_{1/2}$ ), to that corresponding to the prescribed crystallization temperature ( $t_{1/2}$ ) increases with the decrease in  $t_{1/2}$  (Fig. 4).

From above results, the thickness of specimen should be less than 0.05 mm if a rapid crystallization is to be observed down to  $t_{1/2}=1$  sec. The tolerable upper limit of specimen thickness strongly depends on the heat of crystallization: The smaller the heat of crystallization, the larger the limiting value.

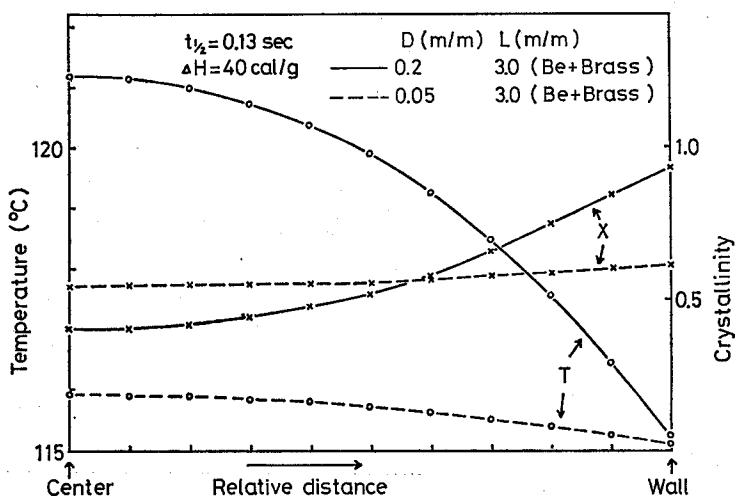


Fig. 3. Calculated degree of crystallinity and temperature distributions in a specimen at the time when the average degree of crystallinity reaches 0.56.

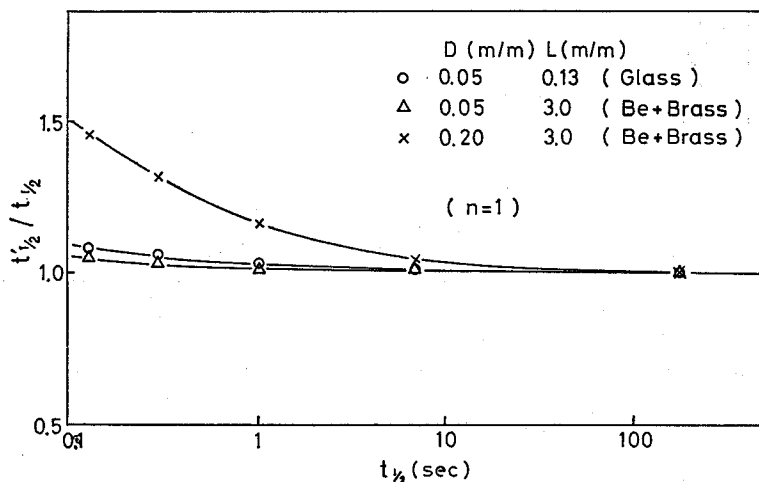


Fig. 4. The ratio of  $t'_{1/2}$  to  $t_{1/2}$ , where  $t'_{1/2}$  is the calculated crystallization half time, and  $t_{1/2}$  is that corresponding to the prescribed crystallization temperature.

### APPARATUS

In order to investigate the crystallization kinetics and the development of structure from oriented melts, a special apparatus was designed and constructed to fulfill the requirements discussed above. A schema of the setup for the measurement of diffracted X-ray intensity during flow-induced crystallization is shown in Fig. 5. With this apparatus, it is possible to heat a thin polymer specimen between beryllium plates ( $50 \mu$  thick) above its melting point, and quench the specimen to a crystallization temperature. Heating and quenching are achieved by a heat gun containing a heat-

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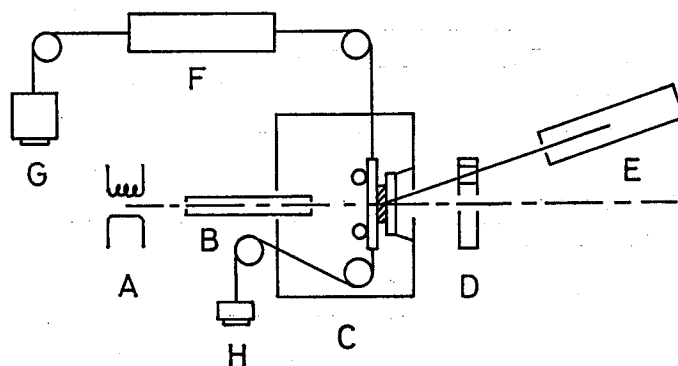


Fig. 5. Schematic diagram of the setup for the measurement of degree of crystallinity with an X-ray counter.

A: X-ray source, B: Collimation system, C: Sample chamber,  
D: Annular slit, E: X-ray counter, F: Differential transformer,  
G: Weight, H: Counter weight.

ing element and a blower. The temperature of the air stream from the gun is regulated by an automatic controller, and reaches its prescribed value within a minute. The temperature of the specimen can be measured by using a thermocouple embedded in one of the two brass bases to which beryllium plates are attached.

First the specimen was melted above its melting temperature and then quenched to a crystallization temperature. After the crystallization temperature was reached, the supercooled specimen was deformed in shear with a load applied to one of the beryllium plates. The other beryllium plate was firmly fixed to the frame of the apparatus. The displacement of the beryllium plate was recorded by means of a differential transformer. During the deformation, the strongest crystalline X-ray diffraction intensity was measured with the aid of an annular slit and a Geiger counter or a scintillation counter. From the measured intensity, the degree of crystallinity  $X(t)$  at time  $t$  was calculated as previously stated.<sup>1)</sup>

To observe the change in X-ray diffraction pattern on a TV screen, we employ a combination of a fluorescent screen, an image orthicon, and a video tape recorder (Rigaku X-ray TV system). However, we do not enter into details here. For the purpose of observing the light scattering pattern which provides structural information in the range of  $1\ \mu\sim 100\ \mu$ , the X-ray source, the beryllium plates, and the X-ray counter in Fig. 5 should be replaced with a He-Ne gas laser, glass slides and a photographic film, respectively, and two polarizing plates are added (Fig. 6).

## EXPERIMENTAL AND RESULTS

The main purpose of the present paper is to point out some requirements of an apparatus for measuring flow-induced crystallization, and to describe the outline of a constructed apparatus to fulfill the requirements. Some results obtained using this apparatus, therefore, are shown here without detailed discussions from a viewpoint of structural formation.

A thin film (0.05~0.1 mm thick) of a high density polyethylene (Sholex 6009) was melted between the beryllium plates at 180°C and heated 10 min. at this temper-

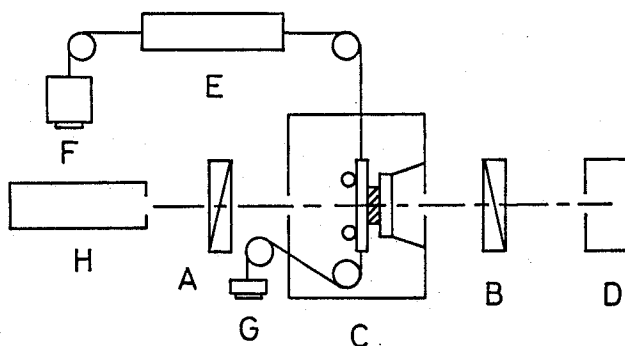


Fig. 6. Schematic diagram of the setup for photographing light scattering patterns during the course of crystallization.

A: Polarizer, B: Analyzer, C: Sample chamber, D: Camera, E: Differential transformer, F: Weight, G: Counter weight, H: He-Ne gas laser.

ature. At the end of heating period, the specimen was quenched to a crystallization temperature of  $125^{\circ}\text{C}$  by altering the setting position of the automatic controller. After the crystallization temperature was reached, the movable plate was loaded, and the integral intensity of (110) diffraction and the displacement of the plate were recorded. From these records, the degree of crystallinity and the shear strain were calculated as functions of time. Results for three different shear stresses are illustrated in Figs. 7a, 7b, 7c. In every case, the rate of crystallization increases with

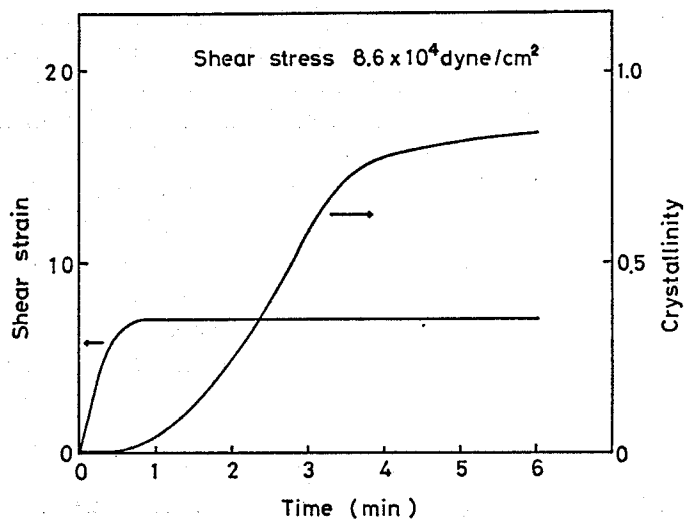


Fig. 7a. Degree of crystallinity and strain vs. time relations after loading. (Sholex 6009) Shear stress:  $8.6 \times 10^4$  dyne/cm<sup>2</sup>.

the shear stress, and the rate of strain rapidly decreases to zero after the initiation of crystallization. These facts are in good agreement with those known in the melt spinning<sup>1)</sup> or film formation process.<sup>2)</sup>



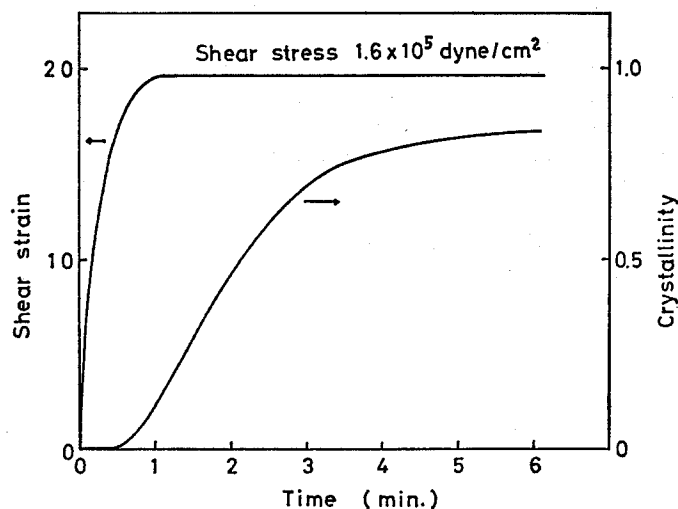


Fig. 7b. Shear stress:  $1.6 \times 10^5$  dyne/cm<sup>2</sup>.

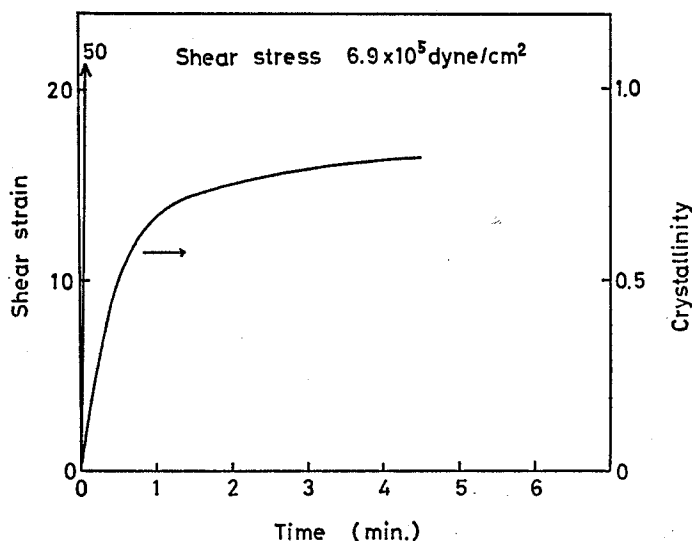


Fig. 7c. Shear stress:  $6.9 \times 10^5$  dyne/cm<sup>2</sup>.

In the present experiment, a sealed off type X-ray tube (tube current 20 mA) was used, and the time constant of the X-ray counting system was 0.5 sec. If a more powerful X-ray generator with a rotating anode (tube current 200~1000 mA) is used, the time constant can be reduced to the order of 0.01 sec. and more rapid crystallization process will be observable.

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